

**PRODUCTION OF BIODIESEL FROM WASTE COOKING OIL AND RBD  
PALM OIL USING BATCH TRANSESTERIFICATION PROCESS**

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of the requirements for the award of the degree of  
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I declare that this thesis entitled “Production of Biodiesel from Waste Cooking Oil and RBD Palm Oil Using Batch Transesterification Process” is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.”

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Dedicated especially to Father, Mother, Brothers and Sisters who give me inspiration  
and support that made this work possible.

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## ABSTRACT

Waste Cooking Oil (WCO) has significant potential as the raw material or starting substance for biodiesel production. The objective of this research is to examine the performance of yield and purity of biodiesel from WCO as the starting material with different catalyst ( $\text{NaOCH}_3$ ) concentration and reaction time via single step batch transesterification process. It is also to investigate the extent to which the sodium methoxide ( $\text{NaOCH}_3$ ) as the catalyst and the effect of batch transesterification process on various parameters in production of biodiesel. The purity of methyl ester content in biodiesel is measured by Gas Chromatography. The exhaust emissions of biodiesel produced were evaluated by combustion test using Gas Combustion Unit. Results indicate that the higher conversion was obtained when RBD palm oil which is 98.2% yield and 97.5% purity instead of 96.8% yield and 94.7% purity in WCO used as the raw material. Biodiesel produced from WCO gives less exhaust emission of CO and  $\text{CO}_2$  compared to commercial diesel thus contributed to the reduction of greenhouse gas that effect the global warming.

## ABSTRAK

Minyak masak terpakai mempunyai potensi sebagai bahan mentah dalam penghasilan biodiesel. Objektif kajian adalah untuk memeriksa kadar hasil dan ketulenan biodiesel yang dihasilkan daripada minyak masak terpakai, dengan kepekatan mangkin sodium metoksida dan masa tindakbalas yang berbeza dalam satu langkah proses transesterifikasi berkelompok. Kajian ini juga adalah untuk menyiasat takat kepekatan mangkin sodium metoksida dan kesan proses transesterifikasi berkelompok ke atas pelbagai parameter dalam penghasilan biodiesel. Ketulenan metil ester di dalam biodiesel diukur dengan Gas Kromatografi. Pancaran buangan daripada biodiesel yang dihasilkan dinilai dengan ujian pembakaran menggunakan Unit Pembakaran Gas. Keputusan menunjukkan penukaran tertinggi diperolehi apabila minyak sawit digunakan sebagai bahan mentah yang mana memberi 98.2% kadar hasil dan 97.5% ketulenan, sebaliknya 96.8% kadar hasil dan 94.7% ketulenan diperolehi jika minyak masak terpakai digunakan sebagai bahan mentah. Biodiesel yang dihasilkan daripada minyak masak terpakai memberi pancaran buangan karbon monoksida dan karbon dioksida yang kurang berbanding diesel komersial, seterusnya menyumbang kepada pengurangan kesan gas rumah hijau yang memberi kesan kepada pemanasan global.

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## CHAPTER 1

### INTRODUCTION

#### 1.1 Overview of Research

With the exception of the hydroelectricity and nuclear energy, the majority of the world energy needs are supplied through petrochemical sources, coal and natural gas. All of these sources are finite and at current usage rates will be consumed in the future (Meher *et al*, 2006). The depletion of world petroleum reserves and increased environmental concerns has stimulated recent interest in alternative sources for petroleum based fuels (Fukuda *et al*, 2001).

Biodiesel, derived from vegetable oil or animal fats by transesterification with alcohol like methanol and ethanol, is recommended for use as a substitute for petroleum based diesel mainly because biodiesel is an oxygenated, renewable, biodegradable and environmentally friendly biofuel with similar flow and combustion properties and also low emission profile (Altin and Selim, 2001). It helps to reduces global warming gas emissions such as carbon dioxide. Biodiesel has no aromatics, almost no sulfur and contains 11% oxygen by weight. This characteristics of biodiesel reduce the emissions of carbon monoxide, hydrocarbon and particulate matter in the exhaust gas compared to petroleum based diesel fuels (Peterson and Hustrulid, 1998).

Currently, compared to petroleum based diesel, the high cost of biodiesel is a major barrier to its commercialization. It is reported that approximately 70%-85% of the total biodiesel production cost arises from the cost of the raw material (Fukuda *et al*, 2001). Use of low cost feedstocks such as waste cooking oil (WCO) should help make biodiesel competitive in price with petroleum diesel. Everywhere in the world, there is an enormous amount of waste lipids generated from restaurants, food processing industries and fast food shops everyday (Mittlebach and Gangl, 2001).

Because of the good properties and the environment improvement, many countries pay much attention to research and development (R&D) of biodiesel industry and constitute favorable legislation for it. More than 2.7 million tons biodiesel in 2003 was made in Europe, and 8-10 million tons is expected in 2010 (Altin and Selim, 2001).

Unfortunately, many of these feedstocks contain large amounts of free fatty acids (FFAs). These FFAs react with alkali catalysts to produce soaps that inhibit the fatty acid methyl esters (FAMES) formation (Gerpen *et al*, 2004). In the case of the vegetable oils that contain up to 5% FFAs, the transesterification reaction can still be catalyzed with an alkali catalyst. However, additional catalyst must be added to compensate for the catalyst lost to soap. This soap can exhibit the separation of the methyl ester and glycerol and also contribute to emulsion formation during the washing step (Gerpen, 2005).

## **1.2 Problem Statement**

The problem was to determine the extent to which the sodium methoxide ( $\text{NaOCH}_3$ ) as the catalyst and the effect of batch transesterification process on various parameters where WCO and RBD palm oil are used as a raw material in production of biodiesel.

### **1.3 Objective of Study**

The objective of this research is to examine the performance of yield and purity of biodiesel from WCO as the starting material with different catalyst ( $\text{NaOCH}_3$ ) concentration and reaction time via single step batch transesterification process.

### **1.4 Scope of Study**

The scopes of this research are:

1. To study the effect of catalyst concentration on yield and purity of biodiesel using batch transesterification process.
2. To study the combustion characteristic of biodiesel from both RBD palm oil and WCO using batch transesterification process and analyze the product using Gas Chromatography.

In the research that we conduct, we used the catalyst concentration of 0.25 to 1.5wt%. While the temperature range used is fixed at 40°C and the time that be conducted is between 20 to 50 minutes.

### **1.5 Rationale and Significances**

The rationale of this research is to identify the important variables and to propose a suitable approach in scaling up the production of biodiesel from RBD palm oil and WCO using batch transesterification process. With the important variables such as catalyst concentration, reaction time, reaction temperature and ratio of methanol to oil used, we can produce high quality of biodiesel which have a high yield and high purity of methyl ester content.

The high energy demand in the industrialized world as well as in the domestic sector, had caused pollution problems due to the widespread use of fossil fuels make it increasingly necessary to develop the renewable energy sources of smaller environmental impact than the fossil fuels such diesel fuels. The alternative fuel must be technically feasible, economically competitive, environmentally acceptable and readily available that is familiar to biodiesel properties. Biodiesel also biodegradable, non-toxic and has low emission profiles as compare to diesel fuel.



## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Historical Background on Biodiesel Production

The first record of the use of vegetable oils as liquid fuels in internal combustion engines is from 1900 when Rudolf Diesel used peanut oil (Shay, 1993). However because of its low cost and easy availability, petroleum became the dominant energy source and petroleum diesel was then developed as the primary fuel for diesel engines. Nonetheless, petroleum and its derivatives fuels have periodically been through short supply and consequently, the search for alternative energy sources has emerged (Zanin *et al*, 2000). At that time the pyrolysis of different triglycerides was also used for liquid fuel supply in different countries. For example, hydrocarbons were produced in China by a tung oil pyrolysis batch system used as liquid fuels (Chang and Wan, 1947). Another approach proposed at this time was the use of fatty acids ethyl or methyl esters, obtained by transesterification or alcoholysis of vegetable oils or esterification of fatty acids combined with transesterification of triglycerides (Keim, 1945).

Biodiesel production is a very modern and technological area for researchers due to the relevance that it is winning everyday because of the increase in the petroleum price and the environmental advantages (Marchetti *et al*, 2005). It is an alternatives fuel for diesel engines that is produced by chemical reaction of a vegetable oils or animal fats with an alcohol such as methanol. The product is called as methyl ester or biodiesel, which is receiving high attention as an alternative, nontoxic, biodegradable and renewable diesel fuels (Ma and Hanna, 1999). When biodiesel displaces petroleum diesel, it reduces global warming gas emission such as carbon dioxide. Biodiesel has no

aromatics, almost no sulfur and contains 11% oxygen by weight. These characteristics of biodiesel reduces the emissions of carbon monoxide, hydrocarbon and particulate matter in the exhaust gas compare petroleum-based diesel fuels (Peterson and Hustrulid, 1998).

Non-food product production from agricultural raw materials is more important than feed protein production in relation to the market economy of Malaysia, which are the biggest palm oil producer and exporter in the world. In 2000, export earnings from palm oil exceeded that from oil products (Malaysia exports some petroleum products after refining) and gas. That has made palm oil the biggest single export revenue earner for the country. Unlike oil and gas, which have a heavy foreign content, palm oil production is virtually 100% local. In 2000, the palm oil industry earned nearly US\$ 6.50 billion in exports and US\$ 7.5 billion in 2001. The Palm Oil Research Institute of Malaysia (PORIM) has taken an initiative since 1988 to look at the possibilities of converting oil palm products into fuels. One of the first products was the use of methyl ester of palm oil as diesel substitute. The use of methyl esters as fuel proved technically to be a very suitable substitute obtained by PORIM, Malaysia. The methyl ester of palm oil is known as palm oil diesel (POD) (Kalam *et. al.*, 2002).

Vegetable oils are widely available from various sources, and the glycerides present in the oils can be considered as a viable alternative for diesel fuel. Biodiesel, which is synthesized from bio-oil, is a realistic alternative of diesel fuel because it provides a fuel from renewable resources and has lower emissions than petroleum diesel. It is biodegradable and contributes a minimal amount of net greenhouse gases or sulfur to the atmosphere. More specifically, biodiesel cuts down on the amount of carbon dioxide, hydrocarbons, and particulate matter released into the environment (Dalai *et. al.*, 2003).

Biodiesel is defined as the monoalkyl esters of long chain fatty acids derived from renewable feed stocks like vegetable oils or animal fats. While most of the properties of biodiesel are comparable to petroleum based diesel fuel, improvement of its low temperature flow characteristic still remains one of the major challenges while

using biodiesel as an alternative fuel for diesel engines. The biodiesel fuels derived from fats or oils with significant amounts of saturated fatty compounds will display higher cloud points and pour points (Bhale *et al.*, 2008).

## **2.2 Raw Material**

There are several sources that can be used as raw material for biodiesel production, such as non-edible oil, animal fats and vegetable oil. However, the vegetable oils extracted from plants that are composed of triglycerides were used because they contain similar fuel properties to diesel fuel except for the higher viscosity and low oxidative stability that must be encountered before being converted into biodiesel. So, the vegetable oils that are mostly used in transesterification reactions include pure plant oils (PPOs) or straight vegetable oils (SVOs) and waste vegetable oils (WVOs) (Knothe *et al.*, 2001).

### **2.2.1 Straight Vegetable Oils (SVO)**

Pure plant oils (PPO) or commonly known as straight vegetable oils are not a by-product of other industries either coming from domestic usage. Actually, the straight vegetable oil is a highly grade oil extracted primarily from plants, usually, seeds of oilseed plants. In addition, these oils are the best starting material compared to waste cooking oils because the conversion of triglyceride to fatty acid methyl ester is high and the reaction time is relatively short (Encinar *et al.*, 2006).

### **2.2.2 Waste Cooking Oils (WCO)**

The feedstock coming from waste vegetable oils or commonly known as waste cooking oils is one of the alternative sources among other higher grade or refined oils. Waste cooking oil is easy to collect from other industries such as domestic usage and restaurant and also cheaper than other oils (refined oils). Hence, by using these oils as the raw material, we can reduce the cost in biodiesel production (Canakci and Van Gerpen, 2001). The advantages of using waste cooking oils to produce biodiesel are the low cost and prevention of environment pollution. These oils, need to be treated before disposal to the environment to prevent pollution. Due to the high cost of disposal, many individuals dispose waste cooking oils directly to the environment especially in rural areas. Encinar (2006) concludes that use of waste cooking oils is an effective way to reduce the cost of biodiesel production.

### **2.3 Solvent**

Sprules and Price (1950), stated that alcohol is primary and secondary monohydric aliphatic alcohols having one (1) to eight (8) carbon atoms. In transesterification process, the main solvent used is alcohol. The examples of alcohol that can be used in the transesterification of triglycerides are methanol, ethanol, propanol, butanol and amyl alcohol. Methanol is the most widely used because of its low price and its physical and chemical advantages (polar and shortest chain alcohol). It can quickly react with triglycerides and sodium hydroxide and easily dissolved in it (Marchetti *et al.*, 2005).

## **2.4 Catalyst**

A catalyst is a substance that accelerates the rate of reaction by lowering its activation energy. A catalyst recovered unchanged and it does not appear in the product. Catalyst used in the transesterification of triglycerides can be classified as homogeneous, heterogeneous and enzyme catalyst. Fangrui Ma and Milford A. Hanna (1999), stated that excess amount of catalyst would lead to the higher amount of production cost and reduce product yield.

### **2.4.1 Homogeneous Catalyst**

Homogeneous catalyst involves processes in which catalyst is in solution with at least one of the reactant. Basically, in this transesterification process, there are two types of homogeneous catalyst which is acid catalyst ( $\text{H}_2\text{SO}_4$  or  $\text{HCl}$ ) and alkali catalyst ( $\text{KOH}$  or  $\text{NaOH}$ ). Homogeneous basic catalyst provides much faster reaction rates than heterogeneous catalyst, but it is difficult to separate homogeneous catalyst from the reaction mixture (Du *et al.*, 2004).

### **2.4.2 Heterogeneous Catalyst**

A heterogeneous catalytic process involves more than one phase, usually the catalyst is a solid and the reactant and product are in liquid or gaseous form. There are many advantages of using heterogeneous catalyst such as non-corrosive, environmental friendly present fewer disposal problems, easier in separation from liquid product and they can be design to give higher activity, selectivity and longer catalyst lifetime (Gryglewicz, 1999). There are many types of heterogeneous catalyst such as alkaline earth metal oxides, anion exchange resins, various alkali metal compounds supported on alumina and various type of zeolite that can be use in various type of chemical reaction

including transesterification process. However, most anion exchange resins and supported alkali metal catalyst are easily corroded by methanol and they exhibit short catalyst lifetime in catalyst transesterification. The alkaline earth metal oxides compound is very favorable used in transesterification process because it is slightly soluble in organic solvents (Supes *et al.*, 2004).

### **2.4.3 Enzyme Catalyst**

There also have a different way of synthesizing biodiesel by using bio-catalyst such as lipase enzyme instead of chemically catalyst. Bio-catalyst such as enzyme is a high molecular weight protein or protein-like substance that acts on substrate (reactant molecule) to transform it chemically at a greatly accelerate rate than the uncatalyzed rate (Shuler nad Kargi, 2002).

## **2.5 Process of Synthesizing Biodiesel**

There are different processes which can be applied to synthesize biodiesel such as direct use and blending, micro emulsion process, thermal cracking process and the most conventional way is transesterification process. However, there are a lot of methods can be done through transesterification process such as based-catalyzed transesterification, acid-catalyzed esterification, intergrated acid-catalyzed pre-esterification of FFAs and based-catalyzed transesterification, enzyme-catalyzed transesterification, hydrolysis and supercritical alcohol transesterification (Saka *et al.*, 2001).

### **2.5.1 Direct Use and Blending**

The direct use of vegetable oils in diesel engine is not favorable and problematic because it has many inherent failings. Eventhough the vegetable oils have familiar properties as biodiesel fuel, it required some chemical modification before can be used into the engine. It has only been researched extensively for the past couple of decades, but has been experimented with for almost hundred years. Although some diesel engine can run pure vegetable oils, turbocharged direct injection engine such as trucks are prone to many problems. Energy consumption with the use of pure vegetable oils was found to be similar to that of diesel fuel. For short term use, ratio of 1:10 to 2:10 oil to diesel has been found to be successful (Ma and Hanna< 1999).

### **2.5.2 Micro-emulsion Process**

Schwab *et al.*, (1987) defined micro-emulsion as colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the  $1 \pm 150$  nm range formed spontaneously from two normally immiscible liquids and one or more ionic or non-ionic amphiphiles. Micro-emulsion with solvents such as methanol, ethanol and 1-butanol has been studied to solve the problem of the high viscosity of vegetable oils. They can improve spray characteristics by explosive vaporization of the low boiling constituents in the micelles.

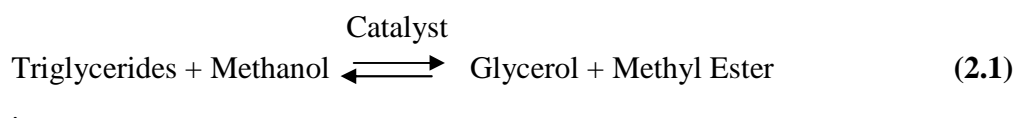
### **2.5.3 Thermal Cracking (Pyrolysis)**

Sonntag, (1979) defined pyrolysis as the conversion of one substance into another by means of heat or heating with the aid of a catalyst. Pyrolysis involves heating in the absence of air or oxygen and cleavage of chemical bonds to yield small molecules (Weist et al., 1979). Pyrolytic chemistry is difficult to characterize because of the variety

of reaction path and the variety of reaction products that may be obtained from the reaction occur. The pyrolyzed material can be vegetable oils, animal fats, natural fatty acids and methyl esters of fatty acids. The first pyrolysis of vegetable oil was conducted in an attempt to synthesize petroleum from vegetable oil (Ma and Hanna, 1999).

#### 2.5.4 Transesterification Process

Transesterification or alcoholysis is the displacement of alcohol from an ester by another in a process similar to hydrolysis, except than alcohol is used instead of water (Srivatava and Prasad, 2000). This process has been widely used to reduce the high viscosity of triglycerides. The transesterification reaction is represented by the general equation as in the following equation. Transesterification is one of the reversible reactions and proceeds essentially by mixing the reactants. However, the presence of a catalyst (a strong acid or base) will accelerate the conversion.



Transesterification of triglycerides with methanol and aid of catalyst produce methyl ester and glycerol. The glycerol layer settles down at the bottom of the reaction vessel. The step wise reactions are reversible and a little excess of alcohol is used to shift the equilibrium towards the formation of esters. In presence of excess alcohol, the forward reaction is first order reaction and the reverse reaction is found to be second order reaction. It was observed that transesterification is faster when catalyzed by alkali (Freedman *et al*, 1986).